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Multiple tracers demonstrate distinct sources of dissolved organic matter to lakes of the Mackenzie Delta, western Canadian Arctic

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Abstract

Lakes of the Mackenzie Delta occur across a gradient that contains three clear end members: those that remain connected to river-water channels throughout the summer; those that receive only brief inputs of river water during an annual spring flood but contain dense macrophyte stands; and those that experience significant permafrost thaw along their margins. We measured dissolved organic carbon (DOC) concentration, dissolved organic matter (DOM) absorption and fluorescence, and stable isotopes of DOM, DOM precursor materials, and bacteria to elucidate the importance of river water, macrophytes, and thermokarst as DOM sources to Mackenzie Delta lakes. Despite standing stocks of macrophyte C that are sevenfold to 12-fold greater than those of total DOC, stable isotopes indicated that autochthonous sources contributed less than 15% to overall DOM in macrophyte-rich lakes. Instead, fluorescence and absorption indicated that the moderate summertime increase in DOC concentration in macrophyte-rich lakes was the result of infrequent flushing, while bacterial $\delta^{13}C$ indicated rapid bacterial removal of autochthonous DOC from the water column. In thermokarst lakes, summertime increases in DOC concentration were substantial, and stable isotopes indicated that much of this increase came from C released as a result of thermokarst-related processes. Our results indicate that these distinct sources of DOM to neighboring arctic Delta lakes may drive between-lake differences in C cycling and energy flow. Rapidly assimilated macrophyte DOM should be an important contributor to microbial food webs in our study lakes. In contrast, the accumulation of thermokarst-origin DOM allows for a significant role in physico-chemistry but indicates a lesser contribution of this DOM to higher trophic levels.

Resolving the relative importance of dissolved organic matter (DOM) from watershed-derived allochthonous and algal-derived autochthonous sources continues to be a focus of limnological study (Cole et al. 2011). Among other things, differences in DOM source and lability can influence its effect on aquatic carbon (C) cycling and food web structure. For example, while allochthonous DOM typically constitutes the bulk of the within-lake pool (Kritzberg et al. 2006), autochthonous, algal-derived DOM tends to be more microbially labile and rapidly incorporated into bacterial biomass (Kritzberg et al. 2006; McCallister et al. 2006).

The significance of other potential DOM sources to the within-lake pool, however, has received much less attention. One possible non-algal source of autochthonous DOM is that derived from macrophyte productivity. Particularly in shallow lakes, macrophytes can occur in extremely dense stands, with productivity rates often exceeding those of algal sources (Wetzel 1992). Both the exudates that occur during photosynthesis (Demarty and Prairie 2009) and the leachates that result from the breakdown of senesced vegetation could render macrophytic organic matter an important source of lake-water DOM. Like autochthonous DOM of algal origin, macrophytic DOM appears to be extremely labile, as assessed by measurements of bacterial production on laboratory-extracted macrophyte leachates (Findlay et al. 1986; Mann and Wetzel 1996). However, like all other forms of DOM, this macrophytic organic matter likely requires a bacterial shunt for it to become available to higher trophic levels because macrophyte tissue tends to be an inaccessible food source for planktonic organisms (Lewis et al. 2000).

An alternate source of allochthonous-like DOM in northern lakes may result from the effects of thermokarst (landscape slumping resulting from permafrost thawing), which is currently increasing at lake margins and across the northern landscape (Smith et al. 2005; Walter et al. 2006). Substantial stores of organic matter exist within the world's permanently frozen soils (Gorham 1991). In freshwater systems, thermokarst exposes aged, previously frozen soils to greatly increased biological activity, which can result in substantial generation of both CH_4 (Walter et al. 2006) and CO_2 (Tank et al. 2009). At the same time, surface soils and vegetation are exposed to within-lake processes as they become covered by water. Given the importance of thermokarst for facilitating the release of previously stored organic matter in a gaseous form, it seems likely that this process could also result in substantial DOM additions to the lakes in which it occurs.

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Here, we use a suite of tracers to quantify the importance of macrophytes and thermokarst to within-lake DOM in the Mackenzie Delta, western Canadian arctic. The Delta contains numerous lakes that are macrophyte rich, strongly affected by thermokarst, or largely unaffected by either of these factors (*see* Study site section). Previous work indicates that macrophyte-rich and thermokarst-affected lakes have elevated concentrations of dissolved organic carbon (DOC) but exhibit lower absorption of downwelling irradiance by DOM, when compared to other waterbodies in the Delta (Gareis et al. 2010). This indicates that DOC released from macrophytes and thermokarst-related processes may augment the within-lake pool in these lakes but that a higher proportion of macrophytic organic matter, which is thought to be relatively clear (Wetzel and Manny 1972; Bertilsson and Jones 2003), or the presence of photodegradation may be decreasing DOM absorption (Gareis 2007).

We coupled standard measures of DOC concentration and DOM absorption with the assessment of DOM fluorescence (as excitation emission matrices [EEMs]) and the $\delta^{13}C$ and $\delta^{15}N$ signatures of DOM and DOM precursor materials to trace the origin of DOM in Delta lakes. We specifically chose these metrics to allow a comprehensive assessment of Delta lake-water DOM: higher DOM absorption is indicative of terrestrial-origin DOC, while lower absorption per unit of DOC can indicate autochthonous-origin DOM or the presence of photobleaching (Osburn et al. 2001). Analysis of DOM fluorescence can resolve the relative importance of autochthonous (as protein-like) and allochthonous (humic and fulvic) components within the DOM pool (Stedmon and Markager 2005).

Stable isotope signatures can further be used to resolve the relative importance of source materials (here, DOM precursors) to an overall mixture (lake-water DOM; Peterson and Fry 1987) and are particularly useful when source materials differ markedly in their isotopic composition. We expected this to be true for DOM precursor materials in Delta lakes, given known differences in fractionation between these end members. In the case of $\delta^{13}C$, allochthonous DOM displays a characteristically $\delta^{13}C$-depleted terrestrial signature ($\sim -27‰$), while increasing boundary layer thicknesses in attached algae and submerged macrophytes reduce isotopic discrimination during photosynthesis and enrich $\delta^{13}C$ (discussed in Hecky and Hesslein [1995]). In macrophyte-rich lakes, the striking CO_2 depletion that occurs progressively through the growing season as a result of rapid photosynthesis (Tank et al. 2009; *see* Study site section, below) can increase phytoplankton CO_2 limitation and again decrease photosynthetic ^{13}C discrimination (Hecky and Hesslein 1995).

In addition to our assessment of the composition of the DOM pool in Delta lakes, we examined bacterioplankton $\delta^{13}C$ signatures in macrophyte-rich and thermokarst-affected lakes to assess the relative contribution of these different DOM sources to bacterial biomass.

Methods

Study site—The Mackenzie Delta is a lake-rich region situated where the Mackenzie River enters the Beaufort Sea of the Arctic Ocean. Each spring, meltwater from southern tributaries flows north to meet the ice still present in this northern delta; the resulting ice breakup effects cause a rapid rise in water levels that allows most Delta lakes to flood. However, because of differences in elevation between lake inflows (sill elevation), some lakes flood for days to weeks, while others remain connected to the river channel throughout the ice-free season (Marsh and Hey 1989; Fig. 1a). High-elevation Delta lakes also do not flush fully during their brief connection to the river: on average, the highest elevation lakes in our study contain 40% floodwater (and thus 60% 'legacy water,' largely derived from previous years' floods) following the spring freshet (Lesack and Marsh 2010). This flooding regime plays a key role in regulating these lakes. Delta lakes have small catchments and are surrounded by permafrost that inhibits subsurface and groundwater flow, while the region receives little precipitation (Marsh 1986). Thus, riverine inputs and catchment-specific snowmelt runoff appear to be the only notable sources of terrigenous DOM to Delta lakes. When high-elevation lakes lose connection with the river, sediments rapidly fall out of suspension and the water column clears. This clarity, coupled with flood-delivered nutrients and the shallow depths of Delta lakes ($z_{mean} \approx$ 1.5 m; Emmerton et al. 2007), creates conditions ideal for submerged macrophyte growth in higher elevation lakes (Fig. 1b), with yearly summer biomass accumulations reaching 350 g m^{-2} (dry weight; Squires et al. 2002). In contrast, suspended sediments in lower elevation, connected lakes remain high throughout the summer, resulting in much lower submerged macrophyte standing stocks. Thus,

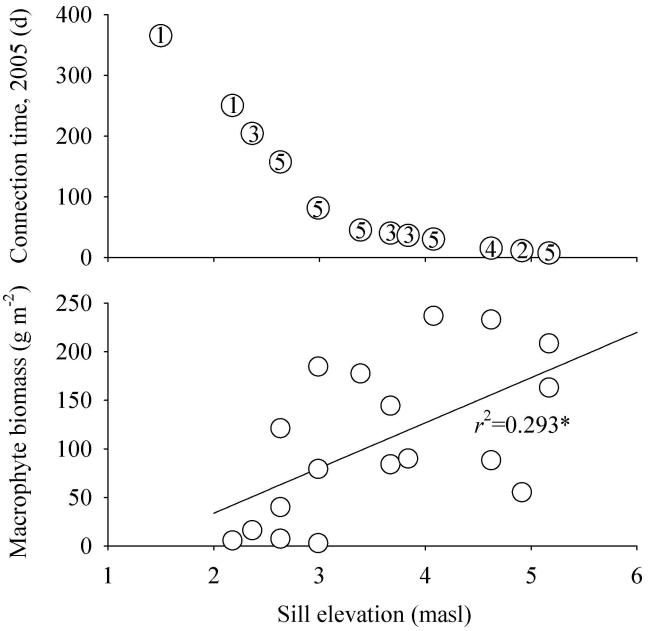

Fig. 1. An overview of surveyed Mackenzie Delta lakes. (a) Connection time and (b) macrophyte biomass across the sill elevation gradient. (a) Multiple lakes share the same sill elevation; the number of lakes at each elevation is indicated inside the symbol. (b) Data are from Squires et al. (2002); not all lakes surveyed for this work were assessed for macrophyte biomass. masl, meters above sea level. * $p < 0.05$.

Delta lakes vary in a predictable manner along the lake elevation gradient: as lake elevation increases, the length (in days) of connection to the system of deltaic river channels decreases, while submerged macrophyte densities increase (Fig. 1). Emergent macrophytes (*Equisetum* sp.) can also occur across the elevation gradient in any lake that possesses significant areas of shallow littoral shelf. In addition, a small subset of high-elevation lakes has been considerably affected by the action of thermokarst after the thawing of ice-rich permafrost below the lake's surface. These lakes do not fit the above-described, regular pattern and are characterized by visible slumps at the lake's edge and mature, dead trees rising vertically through the water column.

Sample collection—We sampled a series of lakes in the east–central section of the Delta chosen to span the lake elevation gradient, with 2005 connection times ranging from 7 to 365 d (Figs. 1a, 2a,b). Samples were collected from a series of 42 lakes (Fig. 2). The full set of 42 lakes was used to collect broad survey-based data, while 15-lake and six-lake subsets were used for more intensive data collections. Sample collection either occurred weekly or over four time periods during the 2005 open water season: the 'spring' (10–17 June), 'early summer' (02–06 July), 'mid-summer' (23 July–08 August), and 'late summer' (22–26 August).

Samples for DOC concentrations and optical absorption by chromophoric DOM (CDOM absorbance) were collected weekly from the six-lake set and in the spring, early summer, and mid-summer from the 42-lake set. Samples for CDOM fluorescence (EEMs) were collected in the spring and late summer from the six-lake set and in the mid-summer from the 15-lake set. Samples to measure stable isotopes ($\delta^{13}C$, $\delta^{15}N$) of DOM precursor materials, $\delta^{15}N$ of DOM, and $\delta^{13}C$ of bacterioplankton were collected from the six-lake set in spring, mid-summer, and late summer. Samples for $\delta^{13}C$ of DOM were collected from the 15-lake set in the spring, early summer, and mid-summer and from the six-lake set in the late summer in order to give greater resolution for $DO^{13}C$. Collection of DOM precursor materials and DOM $\delta^{13}C$ and $\delta^{15}N$ samples always occurred on the same day for any given lake. In addition, river-water samples were collected from a nearby river channel (Big Lake Channel; Fig. 2a) during each sampling period. Samples of Mackenzie River floodwater were collected in late May to early June. We refer specifically to 'river water' and 'floodwater' to acknowledge that floodwater likely accumulates a greater proportion of Delta-origin terrigenous DOM, after being subject to the significant mechanical mixing that occurs during the flood.

Lake-water, river-water, and floodwater samples were collected in clean, acid-rinsed bottles directly beneath the water surface and were immediately transported to the laboratory for processing. Samples were filtered within 8 h of collection using gentle vacuum (0.22 μm, Millipore GSWP, Millipore Corp.). Samples for DOC concentration, CDOM, and $\delta^{13}C$ of DOM were stored in darkness at 4°C until analysis (4 months, 2–4 weeks, and 3 weeks, respectively). Samples for $\delta^{15}N$ of DOM were dried down

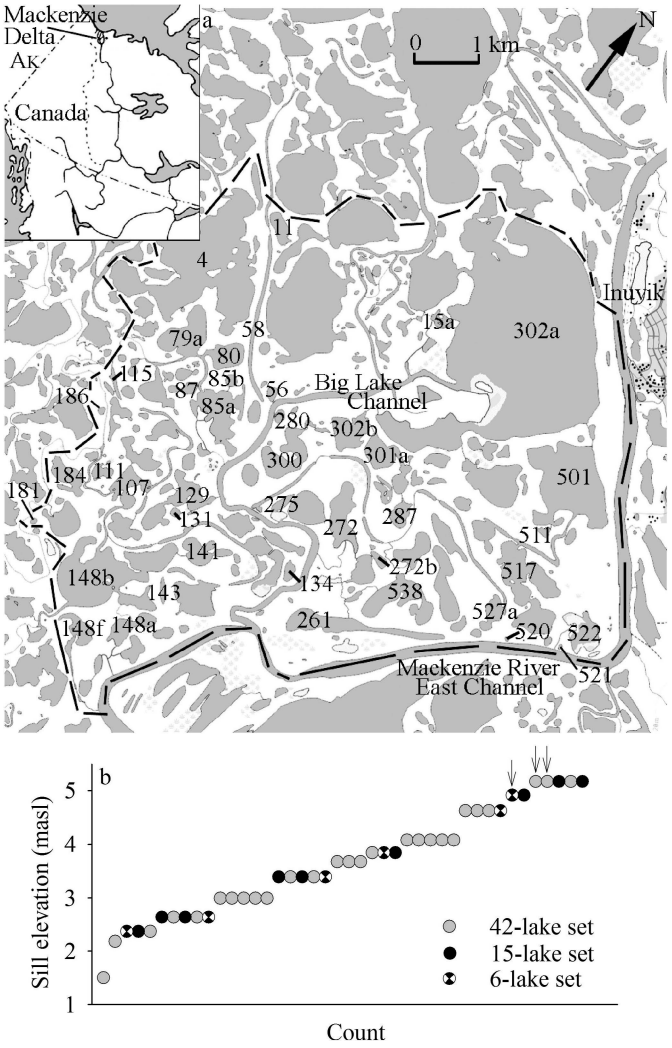

Fig. 2. (a) A map detailing lakes surveyed for this study. Six-lake set, Lakes 129, 80, 87, 280, 56, and 520; 15-lake set, Lakes 4, 141, 148a, 185, 501, 511, 522, 527a, 538, plus the six-lake set; 42-lake set, all indicated lakes; thermokarst lakes, Lakes 520, 181, and 143. (b) The distribution of surveyed lakes across the sill elevation gradient. The smaller surveyed lake sets are subsets of the larger surveyed sets. Arrows indicate thermokarst lakes.

to ~ 10 mL at 60°C and stored frozen until processing and analysis. Samples analyzed for DOC concentration over time showed no degradation, indicating that these storage times did not endanger our results.

DOM precursor materials for isotopic analysis included submerged and emergent macrophytes, seston (for the estimation of algal isotope signatures, described below), and epiphytic algae. Common macrophyte species were collected from each of the six survey lakes and cleaned by repeated rinses in distilled water. Samples for seston were collected by filtering pre-screened (80-μm) water samples through a pre-combusted Whatman GF/F filter (nominal pore size 0.7 μm). Epiphytic algae were collected by vigorously shaking macrophytes in distilled water, using repeated rinses until no algae were visibly dislodged.

Samples for bacterioplankton $\delta^{13}C$ were collected following the method of Kritzberg et al. (2006): bacteria

were cultured in dialysis tubing (SpectraPor 2, 12,000–14,000 Da molecular cutoff, 45-mm flat width) by filling duplicate tubes with 900 mL of 0.22-μm–filtered lake water (Millipore GSWP) combined with 100 mL of grazer-free inoculum (lake water filtered with Whatman GF/A filters, 1.6-μm nominal pore size) and then incubating sealed tubes $\sim$ 20 cm below the water surface. Cultures were harvested after 48 h by filtering replicates through separate pre-combusted GF/F filters. Measures of bacterial production on GF/F-filtered and raw water samples from two of the six sampled lakes indicated that our filtration treatment captured 80–90% of active bacteria in our cultures. A 10-mL subsample of each culture was also preserved with glutaraldehyde (2.5%) to evaluate whether samples were contaminated with phytoplankton or heterotrophic flagellates. Microscopic counts of 4′,6-diamidino-2-phenylindole–stained samples confirmed the absence of these organisms or other types of contamination. All samples for stable isotope analysis were immediately dried at 60°C, at which time they were stored frozen until processing and analysis were performed.

Lake characterization—Sill elevations for all sampled lakes (Marsh and Hey 1988) and submerged macrophyte standing stocks (g dry weight m^{-2}) for a subset of lakes (Squires et al. 2002) were obtained from the literature. A lake's sill elevation determines its connection to the proximate deltaic river channel: when river-water levels fall below the sill elevation, the lake becomes cut off from the river. Connection time (d) to the river for each study lake was estimated by comparing sill elevations to daily river-water levels (Water Survey of Canada online data for hydrometric Sta. 10LC002, Mackenzie River [East Channel] at Inuvik; http://www.wateroffice.ec.gc.ca/index_e.html). The extent of thermokarst around lakes was assessed visually via helicopter during our surveys and confirmed using Google Earth, which was accessed at a resolution of $\sim$ 1 m. Thermokarst extent was scored as the percentage of each lake's shoreline that had collapsed into the lake, assessed as trees sloping toward or falling onto the lake surface. Lakes with greater than 75% thermokarst along their shoreline were considered to be significantly affected by thermokarst for the purposes of this study. Of the lakes classified as 'not significantly affected' by thermokarst, 77% had no visible slumping along their shoreline, and the remaining 23% had an average of 23% ± 9% (95% confidence interval) slumping.

Sample analysis—Samples for DOC concentration were analyzed as non-purgeable organic carbon using a total organic carbon (TOC) analyzer (Shimadzu TOC-V_{csh}, [csh = combustion oxidation, standalone control, high sensitivity], Shimadzu) after sparging for 5 min with 20 mmol L^{-1} HCl (final concentration). CDOM absorbance was measured relative to distilled–deionized water using a Genesys 5 scanning spectrophotometer (Milton Roy) and a 5-cm quartz cuvette. Duplicate scans from 250 to 750 nm (1-nm interval) were performed. Absorption coefficients [$a(\lambda)$] are reported in m^{-1}. We present results for specific ultraviolet absorbance at 254 nm ($SUVA_{254}$ = absorbance(254)/DOC) as a measure of DOM aromaticity (Weishaar et al. 2003) and the $a(250):a(365)$ ratio as a proxy for DOM molecular weight, where higher ratios are indicative of a lower molecular weight DOM pool and, thus, either autochthonous or degraded DOM (Strome and Miller 1978). CDOM fluorescence was measured using a Shimadzu RF-5301 spectrofluorometer with excitation wavelengths ranging from 250 to 450 nm (sampled every 5 nm) and emission wavelengths ranging from 300 to 600 nm. DOM fluorescence values were corrected for scattering effects by MilliQ water blank subtraction and for inner filter effects and were normalized to the water Raman fluorescence, as described in Boyd and Osburn (2004). Units of fluorescence are, thus, Raman units (nm^{-1}).

Samples for $\delta^{13}C$ of DOM were analyzed following the method of Osburn and St.-Jean (2007); we injected samples into an OI Analytical model 1010 wet oxidation TOC analyzer (OI Corporation), which was modified to allow vented CO_2 to be tapped and redirected to a DeltaPlusXP continuous-flow isotope ratio mass spectrometer (CF-IRMS; Thermo Finnigan) via an electrolytic copper scrubber, water trap, and a Poraplot gas chromatography column to separate N_2 gas and to focus the CO_2.

Samples for $\delta^{15}N$ of DOM were acidified to pH 2, dialyzed using a 100-Da membrane (SpectraPor cellulose ester membrane, Spectrum Laboratories) in a continuous-flow system (to remove dissolved inorganic nitrogen from the sample; Lee and Westerhoff 2005), and lyophilized. Samples for $\delta^{13}C$ and $\delta^{15}N$ of macrophytes and epiphytic algae were ground to a fine powder using a mortar and pestle, and powdered samples were acidified using 2 mol L^{-1} HCl to remove carbonates. Acidified, dried samples of DOM, macrophytes, and epiphytic algae were then weighed into tin capsules (Elemental Microanalysis). Filtered samples were exposed to concentrated HCl vapor overnight to remove carbonates. Seston samples were folded into tin capsules after the top layer of the filtered sample had been separated from the remaining filter and were then analyzed for $\delta^{13}C$ and $\delta^{15}N$. Bacterioplankton samples were folded into tin capsules and analyzed for $\delta^{13}C$ only, because ^{15}N fractionation by bacteria could be substantial, depending on N abundance (Peterson and Fry 1987). Samples were analyzed by the G. G. Hatch Stable Isotope Laboratory (University of Ottawa, Canada) using a Vario III elemental analyzer (Elementar) coupled to a DeltaPlus XP CF-IRMS via a ConFlo II interface.

Data analysis—Fluorescence modeling: The collected EEMs were analyzed using parallel factor analysis (PARAFAC), following the method of Stedmon et al. (2003). PARAFAC resolves the fluorescence signal of the complex DOM pool into separate fluorophores with characteristic excitation emission curves and can be used to extract fluorophores characteristic of both allochthonous and autochthonous DOM (Stedmon and Markager 2005). The PARAFAC analysis was performed using the N-way toolbox 3.10 (Andersson and Bro 2000) in MATLAB® 7.5 (Mathworks). The model was initialized with randomized orthagonalized values, and non-negativity constraints were applied to each dimension. The appropriate number

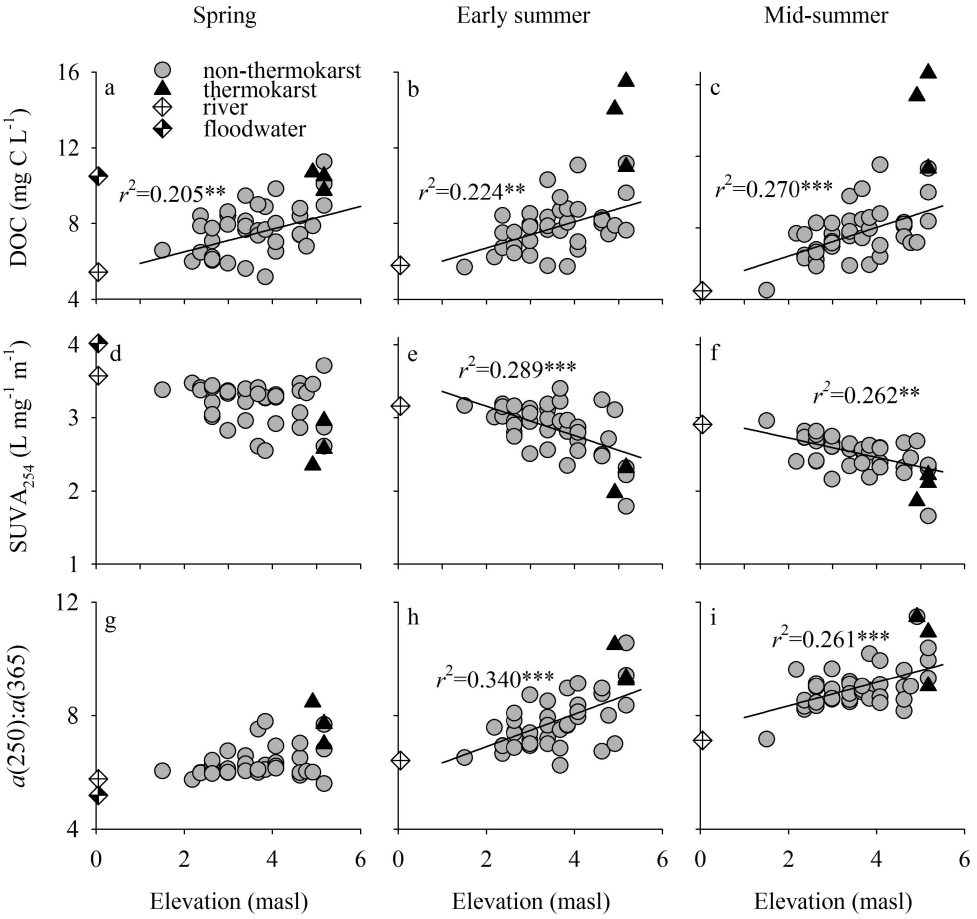

Fig. 3. (a–c) DOC concentration; (d–f) $SUVA_{254}$; and (g–i) inferred molecular weight [$a(250):a(365)$] for 42 Mackenzie Delta lakes surveyed in spring, early summer, and mid-summer. Note that increasing $a(250):a(365)$ is indicative of decreasing molecular weight. Lines indicate a significant correlation; * $p < 0.05$; ** $p < 0.01$; *** $p < 0.001$.

of components of the model was determined using split-half analysis, wherein the data set is divided into two random, equally sized groups; PARAFAC is performed on both halves; and the number of components is limited to those that provide the same loadings in both models (Stedmon et al. 2003). Results of the PARAFAC model are expressed as the maximum fluorescence of each component in a given sample (F_{max} [nm^{-1}]; Stedmon and Markager 2005). Within components, variation in F_{max} across samples corresponds to variations in concentration. However, because different components have different concentration-specific fluorescence intensities, the absolute difference in F_{max} between components is not equivalent to their absolute differences in concentration.

Estimation of phytoplankton isotopic signatures: Phytoplankton $\delta^{13}C$ was estimated using two different methods. For the first, we assumed that seston organic matter was composed entirely of phytoplankton, and we used the seston signature as a phytoplankton proxy. Given that many of these lakes have low inputs of allochthonous particulate organic C (POC; Squires and Lesack 2003), and given that sestonic C : N molar ratios across all lakes (ranging from 5.5 and 7.0) were close to ratios expected for phytoplankton, this seems reasonable for Mackenzie Delta lakes. However, to confirm the validity of our phytoplankton estimates we used the mixing model of Bade et al. (2006) to calculate adjusted phytoplankton $\delta^{13}C$ values, based on measured chlorophyll *a* (Chl *a*) concentrations, published C : Chl *a* ratios (Ramlal et al. 1991), and POC concentrations (Anema et al. 1990) for Delta lakes and assuming a terrestrial end member $\delta^{13}C$ of −28‰. As a result of problems associated with calculating $\delta^{13}C$ fractionation factors for mixed phytoplankton assemblages at variable CO_2 concentrations in situ (Bade et al. 2006; Marty and Planas 2008), we chose to not calculate phytoplankton $\delta^{13}C$ using measured $DI^{13}C$ values in association with fractionation estimates, as has been done elsewhere. $DI^{13}C$ data for these lakes are available in Tank (2009).

Results

DOC concentration across a gradient of Delta lakes—DOC concentration consistently increased with increasing lake elevation in each of the spring, early summer, and mid-summer surveys (Fig. 3a–c). However, increasing submerged macrophyte densities were not associated with higher DOC in any of the surveys (data not shown; $p =$

0.250, 0.171, and 0.177 for spring, early summer, and mid-summer, respectively). In thermokarst lakes, DOC concentration was similar to concentrations in non-thermokarst lakes in the spring, but it rose rapidly in the early season (Fig. 4a), such that summertime DOC was considerably elevated in lakes experiencing thermokarst activity (Fig. 3b,c). DOC concentrations in other high-elevation lakes rose slightly as the summer progressed, while concentrations in lower elevation lakes remained steady or dropped slightly through the summer (Fig. 4a,b). Floodwater DOC concentration was near the high end of the range found for lake water, while river DOC tended to be at or below the concentration found in the lowest elevation Delta lakes (Fig. 3a–c).

CDOM absorbance—$SUVA_{254}$ was not correlated to lake elevation in the spring (Fig. 3d), but it declined significantly with increasing lake elevation in the early summer and mid-summer surveys (Fig. 3e,f). The relationship between $SUVA_{254}$ and DOC concentration was similar to that with lake elevation: in the spring and early summer, $SUVA_{254}$ showed no relationship with DOC concentration (data not shown; $r^2 = 0.040$, $p = 0.121$; $r^2 = 0.000$, $p = 0.654$), while in the mid-summer survey, lakes with the highest concentration of DOC had the lowest DOC-specific absorbance(254) ($r^2 = 0.116$, $p = 0.019$).

Summertime $SUVA_{254}$ also decreased as within-lake submerged macrophyte density increased ($r^2 = 0.186$, $p = 0.042$; $r^2 = 0.168$, $p = 0.051$ for early summer and mid-summer surveys, respectively). In our intensively surveyed lakes, $SUVA_{254}$ declined consistently as the summer progressed, with a sharp drop occurring in mid- to late June (Fig. 4c,d). In contrast to the DOC concentration results, $SUVA_{254}$ from thermokarst was comparable to that found in non-thermokarst waterbodies (Fig. 3d–f). Throughout the summer, $SUVA_{254}$ values for floodwater and river water were similar to, or greater than, those in the lowest elevation Delta lakes.

DOM molecular weight, as inferred from $a(250):a(365)$ ratios, decreased in all lakes as the summer progressed (Figs. 3g–i, 4e,f). Similar to the trends for $SUVA_{254}$, springtime molecular weights did not differ across the lake elevation gradient (Fig. 3g). However, by summertime, inferred DOM molecular weight decreased significantly with increasing lake elevation (Fig. 2h,i). Again, DOM from thermokarst lakes did not differ significantly from this overall pattern, while molecular weights of floodwater and river-water DOM were consistently similar to, or greater than, those found in lower elevation surveyed lakes (Fig. 3g–i). Spring and early summer, but not mid-summer, molecular weights decreased with increasing submerged macrophyte density ($r^2 = 0.159$, $p = 0.057$; $r^2 = 0.286$, $p = 0.013$; and $r^2 = 0.000$, $p = 0.708$, respectively).

CDOM fluorescence—The PARAFAC model resolved three components from our EEM data set. Figure 5a–c compares measured and modeled EEMs for a sample of floodwater DOM and the residuals from this comparison. Residual values were well below those of modeled and measured spectra (maximum residuals were 17-fold lower

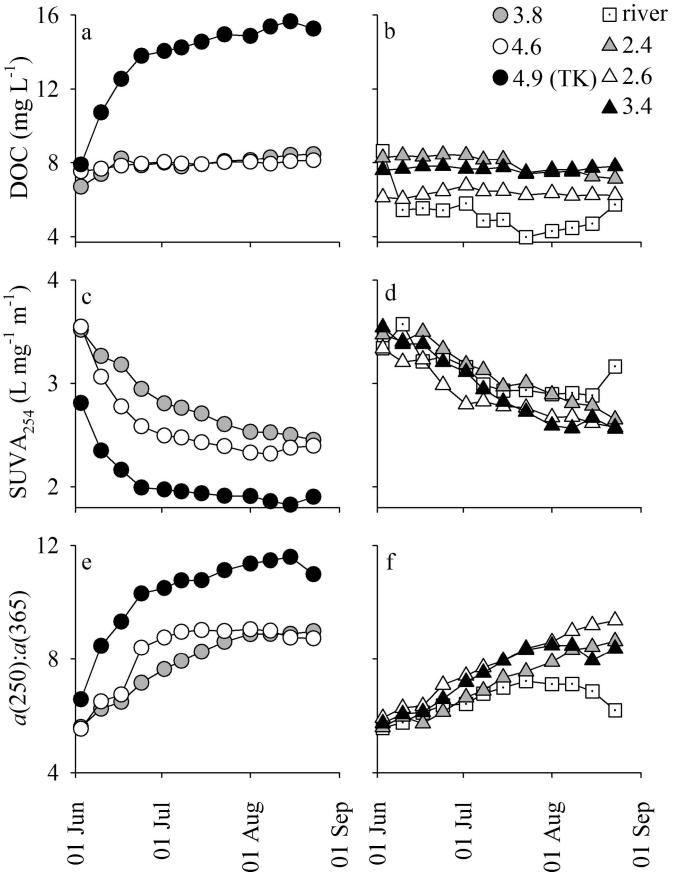

Fig. 4. Weekly values of (a, b) DOC concentration; (c, d) $SUVA_{254}$; and (e, f) inferred molecular weight [$a(250):a(365)$] for river water and the series of six intensively studied lakes. Note that increasing $a(250):a(365)$ is indicative of decreasing molecular weight. Lake sill elevations are indicated in the figure legend.

than measured and modeled values for the comparison shown in Fig. 5). The PARAFAC model explained 99.7% of the variation in our measured EEM spectra.

Of the three components extracted (Fig. 5d–f), component 1 was characteristic of a humic peak, component 2 was characteristic of a fulvic peak, and component 3 was characteristic of a protein-like peak (Stedmon and Markager 2005). F_{max} values for the extracted components did not differ significantly across the gradient of lake elevations (data not shown). When the F_{max} of each component was normalized to DOC concentration (F_{max} : DOC), however, several significant trends emerged. Within lakes, F_{max} : DOC declined as the season progressed for all three components (Fig. 6a–c). F_{max} : DOC also decreased with increasing lake elevation, marginally in the spring and significantly in the mid-summer for component 1 and during all surveys for component 2 (Fig. 6a,b). Although F_{max} : DOC for component 3 appeared to be highest in mid-elevation lakes (Fig. 6c), unimodal (quadratic) regressions were not significant. However, DOC-normalized component 3 did decline significantly with increasing lake elevation in the mid-summer (Fig. 6c). As with CDOM absorbance, the thermokarst lake within this sampled set showed fluorescence values similar to those for non-

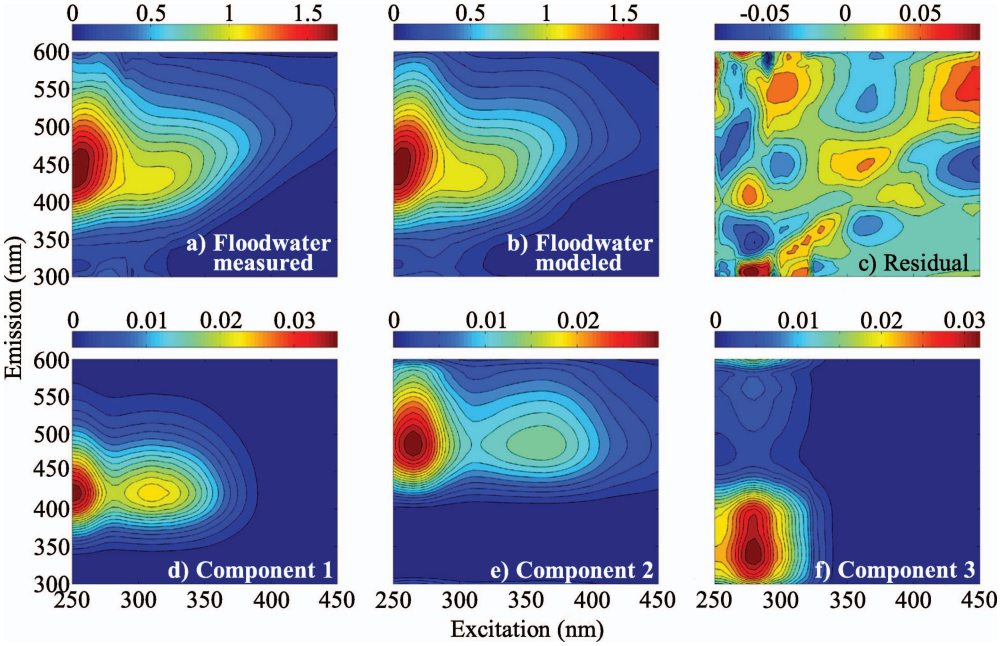

Fig. 5. Results of the PARAFAC analysis for measured EEMs from Delta lake– and river water. (a–c) Measured and modeled floodwater sample, and the residuals of this model. Note the differences in scale across these panels. (d–f) The three components extracted from the PARAFAC model. Component 1 is characteristic of a humic peak, component 2 is characteristic of a fulvic peak, and component 3 is characteristic of a protein-like peak.

thermokarst lakes. For components 1 and 2, DOC-normalized F_{max} values for floodwater and river water were greater than those observed within lakes, while for component 3, floodwater and river-water F_{max} : DOC tended to be lower than for lake water (Fig. 6a–c).

There were also clear trends in the relative contribution of components 2 and 3 to the total CDOM fluorescent signal (Fig. 6d–f). The percent contribution of component 2 to the CDOM fluorescent pool tended to be highest in the spring, while the percent contribution of component 3 tended to be highest in the mid-summer and late summer. The importance of component 2 declined significantly with increasing lake elevation in the spring and mid-summer and declined marginally with increasing lake elevation in the late summer (Fig. 6e). This decline across the lake elevation gradient was compensated for by increases in the relative importance of component 3, which increased significantly with increasing lake elevation in the early summer and mid-summer (Fig. 6f). There were no significant trends in the total F_{max} fluorescent signal.

Stable isotope signatures and mixing models—$\delta^{13}C$ for river-water and floodwater DOM were close to those values typical of terrestrially derived C, ranging from −25.5‰ to −27.1‰. The isotopic $\delta^{13}C$ signature for within-lake DOM closely overlapped these values. In the spring, early summer, and mid-summer, DOM $\delta^{13}C$ ranged from −25.3‰ to −27.8‰ in non-thermokarst lakes, and it did not vary across the lake elevation gradient (data not shown). This was similar to the range in DOM $\delta^{13}C$ values observed during the late summer surveys (Fig. 7). DOM $\delta^{13}C$ for the thermokarst lake included in this survey was slightly $\delta^{13}C$ depleted in comparison to river water, ranging from −27.2‰ to −28.3‰ across all survey dates. Within each survey period, the $\delta^{13}C$ of DOM from the thermokarst lake was always the most depleted of any of the measured lake water signatures.

Generally there was good separation between the $\delta^{13}C$ and $\delta^{15}N$ signatures of various DOM source materials (Fig. 7a–f). Signatures for submerged macrophytes and epiphytic algae were strongly ^{13}C enriched. In submerged macrophyte-rich lakes (shown in Fig. 7c–e), sestonic $\delta^{13}C$ became increasingly enriched as the summer progressed. Calculated phytoplankton $\delta^{13}C$ showed a stronger gradient of ^{13}C enrichment with increasing macrophyte biomass (data not shown). For all lakes in the spring (prior to the onset of macrophyte growth) and in macrophyte-poor lakes throughout the summer, calculated phytoplankton $\delta^{13}C$ was similar to or depleted in comparison to sestonic $\delta^{13}C$ (−6.20 to 0.62). For macrophyte-rich lakes in the summer, calculated phytoplankton $\delta^{13}C$ was similar to or enriched in comparison to sestonic $\delta^{13}C$ (−0.04 to 6.85). Values for emergent macrophytes, which obtain their CO_2 from the atmosphere, were terrestrial like (Fig. 7a,d,e). Across all lakes, signatures for river-water and floodwater DOM and lake-water DOM showed close overlap on our isotopic biplots, while autotrophic end members lay much more distant from lake-water DOM in biplot space.

Within lakes, the lake-water DOM signature fell in the center of the polygon that bounded the DOM source materials on the isotopic biplot, and, thus, multiple source mixing models cannot provide a well-constrained estimate of the contribution of the numerous DOM source types to the lake-water DOM pool (Phillips and Gregg 2003).

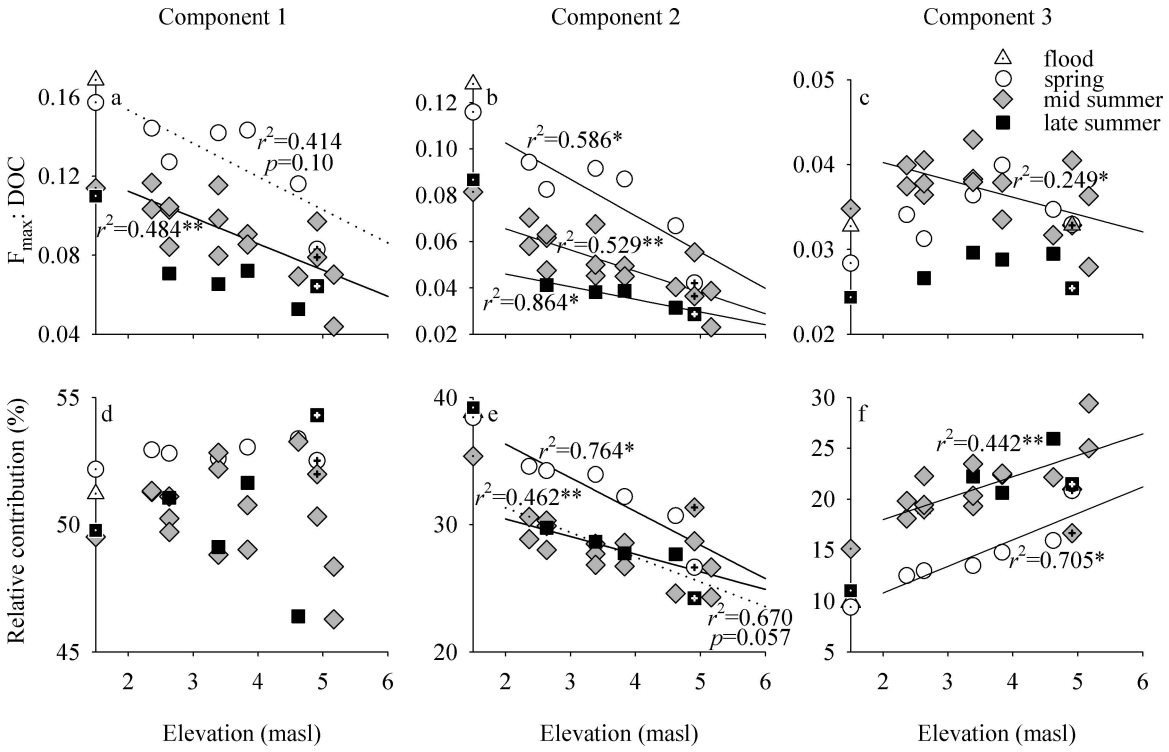

Fig. 6. F_{max} : DOC and the relative contribution to the overall fluorescent pool for the three components extracted from our PARAFAC model: (a, d) Component 1; (b, e) component 2; and (c, f) component 3. Samples for floodwater (dotted triangles), spring (open circles), mid-summer (gray diamonds), and late summer (black squares) are shown in each panel. River-water samples for spring, mid-summer, and late summer are shown with dotted symbols that correspond to the lake-water samples from that time period. Crossed symbols indicate samples from a thermokarst lake. Significant relationships with sill elevation are designated using solid regression lines. Marginal relationships are designated with dotted regression lines, and the corresponding p-value is indicated. Regression analyses do not include river-water and floodwater samples. Significance levels are as in Fig. 3.

Therefore, we used a simplified model that assessed only the contribution of floodwater and submerged macrophytes to lake-water DOM, using only $\delta^{13}C$. We did this only for macrophyte-rich lakes (Fig. 7c–e), in which submerged macrophytes contribute at least 90% to whole lake primary production, yearly primary production rates are relatively high ($\geq$100 g C m^{-2} yr^{-1}; Squires et al. 2009), and lakes do not receive river water after the yearly flood pulse subsides. Thus, it seemed reasonable to assume that macrophytes and floodwater were the primary contributors to within-lake DOM in these waterbodies. Using the full range of submerged macrophyte $\delta^{13}C$ values within each lake, we found that the potential contribution of macrophyte organic matter to within-lake DOM ranged from 1% (Fig. 7d) to a maximum value of 15% (Fig. 7c). In lower elevation lakes (Fig. 7a,b) primary production is much lower (10–20 g C m^{-2} yr^{-1}; Squires et al. 2009), and lakes continue to receive riverine DOM as a result of continued connection to river channels throughout the ice-free season, indicating that the contribution of macrophytes to within-lake DOM should be even less.

In contrast to the DOM results, bacterial $\delta^{13}C$ in non-thermokarst lakes was consistently ^{13}C enriched compared to both the river-water and within-lake DOM signatures (Fig. 7, gray shading). Consequently, simple floodwater and macrophyte end member mixing models indicated that bacteria were preferentially assimilating autochthonous C. In macrophyte-rich lakes, the contribution of macrophyte organic matter to bacterial biomass was estimated to range from a minimum of 12% (Fig. 7d) to a maximum of 68% (Fig. 7c). In thermokarst lakes, both DOM and bacterial biomass appear to be predominantly composed of allochthonous C (Fig. 7f).

Discussion

Macrophyte organic matter is strongly underrepresented in the DOM pool—In macrophyte-dominated shallow lakes, it has been proposed that autochthonous C should comprise a significant proportion of the DOM pool (Briggs et al. 1993; Mann and Wetzel 1995). Photosynthetic exudates from macrophytes have been estimated at 56 μg C g dry weight^{-1} h^{-1} (Demarty and Prairie 2009), while leaching from senesced vegetation could also add significant DOM to the water column (Findlay et al. 1986; Mann and Wetzel 1996). In high-elevation Delta lakes, the per-volume standing stock of submerged macrophyte C is sevenfold to 12-fold that of DOC concentrations (calculations based on Squires et al. 2002; Squires and Lesack 2003), while photosynthesis by submerged macrophytes and their associated epiphytes is rapid enough to drive water column pCO_2 close to zero (Hesslein et al. 1991;

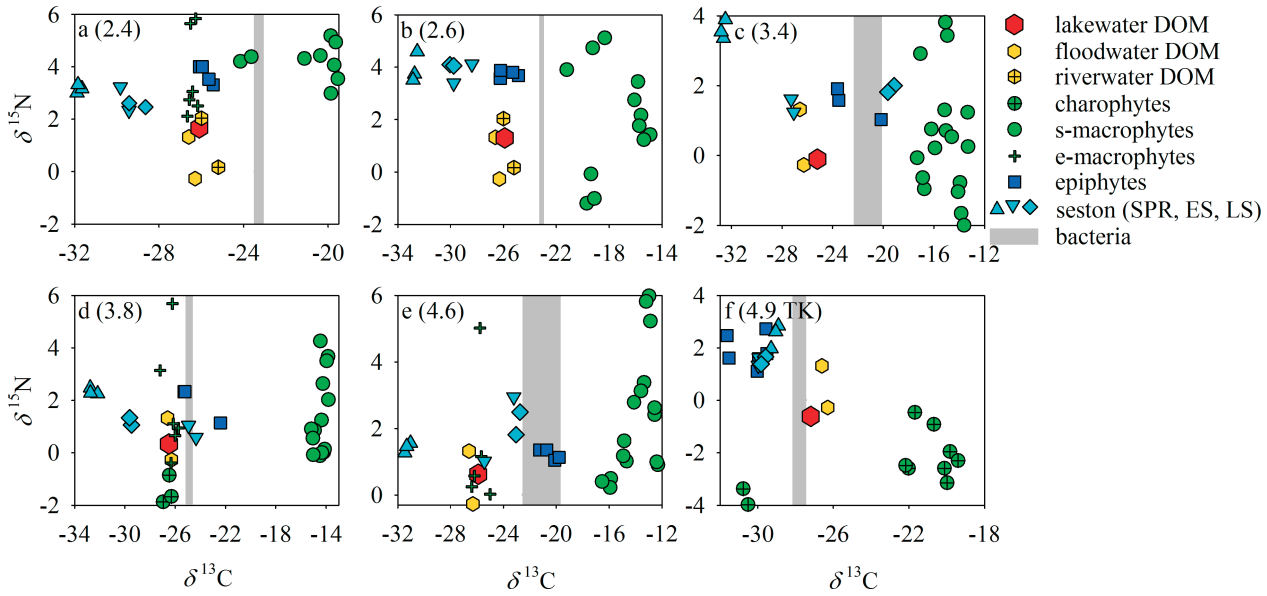

Fig. 7. Biplots of $\delta^{13}C$ and $\delta^{15}N$ for DOM and DOM source materials. Lakes are shown in separate panels, with lake sill elevation (in meters) given in each panel. The thermokarst lake is indicated as (TK). Shown are isotopic values for lake-water DOM (late summer only); floodwater DOM; river-water DOM; charophytes; submerged (s-) macrophytes; emergent (e-) macrophytes; epiphytes; and spring (SPR), early summer (ES), and late summer (LS) seston. Bacterial $\delta^{13}C$ is indicated with gray shading. River water is only shown for lakes that retained connection with the river post-flood (a, b). Emergent macrophytes and charophytes do not occur in all lakes.

Tank et al. 2009). Thus, it seems reasonable that this autochthonous C would be an important contributor to DOM in these lakes.

Our suite of tracers indicates that macrophyte DOM is rapidly assimilated by bacteria (as discussed below) and forms at most a modest component of the bulk DOM pool. Stable isotopes, in particular, indicate that terrestrial or terrestrial-like DOM dominates DOM standing stock across the lake elevation gradient, with simple mixing models indicating that macrophytic DOM accounts for less than 15% of the total pool size in macrophyte-rich lakes. DOM values were very slightly enriched relative to riverine DOM in some macrophyte-rich waterbodies (Fig. 7c,e, enrichment of 0.7–1.4‰), which is consistent with the incorporation of some macrophyte or epiphyte organic matter into the bulk pool. However, a portion of this isotopic enrichment could also be the result of photodegradation, which can enrich DOM $\delta^{13}C$ through selective photolytic decomposition (Osburn et al. 2001; Vähätalo and Wetzel 2008) and is common in hydrologically isolated Delta lakes (Gareis 2007).

Reductions in absorption per unit DOC, molecular weight (Osburn et al. 2001), and humics and fulvics (Moran et al. 2000) are also all well-described consequences of DOM photolysis. These characteristics could also be consistent with macrophyte photosynthetic exudates contributing to the DOM pool in high-elevation Delta lakes: macrophytic DOM has been suggested to be relatively clear and largely composed of simple, low-molecular-weight molecules (Wetzel and Manny 1972; Bertilsson and Jones 2003). However, several lines of evidence indicate that photolysis, rather than the presence of macrophytic DOM, is predominantly structuring DOM spectral quality in these macrophyte-rich lakes: (1) $SUVA_{254}$ and DOM molecular weight declined most rapidly in mid-June, when incident solar radiation is highest. In contrast, rapid macrophyte photosynthesis does not begin until late June in these lakes and continues throughout the summer (Tank et al. 2009). (2) The relative contribution of fulvic-like component 2 to overall F_{max} decreased with increasing lake elevation and, thus, with hydrologic isolation, while humic-like component 1 showed no trend. This agrees well with previous observations that fulvic-acid–like fluorescence is likely more photolabile than humic-acid–like fluorescence, as a result of its longer wavelength excitation and emission features: both longer wavelength fluorescence and absorbance have been shown to be more susceptible to photobleaching than are shorter wavelengths (Hayakawa et al. 2003; Osburn et al. 2009). (3) Previous experimental exposure of Delta lake water to natural sunlight resulted in DOM absorbency losses on the order of 6% over an 8-h incubation period (but no decrease in DOC concentration; Gareis 2007), rates which could certainly account for the relatively low-molecular-weight, transparent DOM observed in high-elevation Delta lakes.

It seems likely that processes directly related to the hydrologic isolation of macrophyte-rich Delta lakes also account for the high DOC concentrations observed in these lakes. High-elevation, macrophyte-rich Delta lakes have a negative water balance between flooding events (Marsh and Lesack 1996) that can decrease water levels by ~ 2 mm d^{-1} after loss of river connection (Marsh 1986) in lakes with a z_{mean} of $\sim$ 1.5 m. This indicates a significant role for evaporative concentration in these lakes, which are typically not fully flushed by the river during the spring flooding event (Lesack and Marsh 2010). In other lake regions, hydrologically isolated lakes have remarkably high DOC concentrations (Curtis and Adams 1995). Delta lakes

also receive a pulse of relatively high-DOC floodwater, as well as inputs of other potentially DOC-rich material that exhibit a terrestrial-like $\delta^{13}C$ signature, including post-flood runoff (rill water; L. Lesack unpubl.) and, in some lakes, the decomposition products of emergent macrophytes. While these inputs are likely to be contained within high-elevation waterbodies, lower elevation lakes continue to be flushed periodically with river water throughout the ice-free season. Finally, trends in DOC concentration correlate strongly with lake elevation, but not with submerged macrophyte biomass, indicating strongly that factors specifically related to hydrologic isolation and evaporation are driving trends in DOC concentration in these lakes.

The fate of autotrophic organic matter in Mackenzie Delta lakes—Bacterial $\delta^{13}C$ signatures indicate that preferential assimilation of autochthonous DOM by bacteria acts as a sink for macrophyte DOM in these lakes, as has been shown in systems in which primary productivity is dominated by phytoplankton (Kritzberg et al. 2006; McCallister et al. 2006). Given that macrophytic organic matter is largely absent from the bulk DOM pool, this indicates that the flux of this DOM into biomass may be extremely rapid. Like that of phytoplankton origin, DOM derived from macrophyte leachates is an extremely labile bacterial substrate, supporting high rates of bacterial production and growth efficiency (Findlay et al. 1986; Mann and Wetzel 1996). In accordance with these stable isotope observations, CDOM fluorescence data indicate that the DOM pool becomes proportionately more labile with increasing lake elevation and macrophyte density, based on increasing proportions of protein-like DOM within the overall pool. Protein-like DOM fluorescence has been attributed both to recent bacterial activity (Cammack et al. 2004) and to the presence of autochthonous DOM (Stedmon and Markager 2005), indicating continued inputs of fresh DOM in these waterbodies. Another potential sink for macrophyte-derived DOM is sequestration before it reaches the pelagic zone. The rapid cycling that we observe between autochthonous DOM and bacterioplankton in the water column likely also occurs on macrophyte and sediment surfaces: bacteria colonizing the epiphytic and epipelic mats that occur on standing, and senesced, macrophytes may consume a large proportion of macrophyte exudates and leachates before this DOM enters the water column.

The importance of thermokarst to DOM in Delta lakes—In contrast to our results for macrophytic DOM, several lines of evidence indicate that thermokarst causes organic matter from permafrost or nearshore soils and vegetation to form an important component of the within-lake DOM pool. The remarkably high DOC observed in thermokarst lakes was terrestrial in origin, as indicated by the $\delta^{13}C$ signatures of both DOM and bacteria. At the same time, the factors proposed to be augmenting terrestrial or terrestrial-like DOM in macrophyte-rich lakes are not proportionately greater in lakes experiencing thermokarst. In the Mackenzie Delta, thermokarst tends to be prominent in high-elevation waterbodies, and thermokarst lakes are therefore poorly connected to the river. Thus, evaporation is certainly an important component of the water budget of these lakes. However, the thermokarst lakes in our study had an average lake depth that was about 0.5 m greater than the overall average depth for Delta lakes, as a result of the lake deepening caused when ice-rich permafrost thaws below the lake bed. Presumably this decreases the relative importance of evaporative concentration in these lakes, as a result of increased volume to surface area ratios. Furthermore, flushing rates and the input of floodwater and post-flood runoff to thermokarst lakes should be similar to that of other non-thermokarst, high-elevation lakes. Finally, the steep lake margins in these relatively deep lakes cause emergent macrophytes to occur only sparsely in these waterbodies and, thus, to be unable to contribute substantial organic matter to these lakes. DOM $\delta^{13}C$ from the intensively studied thermokarst lake was also closer to the standard terrestrial endpoint ($-28‰$ to $-29‰$) than was the river-water DOM signature, indicating some input of autochthonous DOM to the river-water pool and an enhanced proportion of terrestrial DOM in the thermokarst lake-water pool. Because phytoplankton biomass in our intensively studied thermokarst lake is extremely low ($< 1\%$ of the DOM pool, per unit of carbon), this autochthonous C source is unlikely to account for the $\delta^{13}C$ shift that we observe. Thus, the contribution of permafrost C or of C from more contemporary soils and vegetation that have slumped into the lake seems the most likely explanation for the enhanced DOC observed in Delta thermokarst lakes.

The consequences of diverse DOM sources to Delta lakes—The divergent fates of different DOM sources in Mackenzie Delta lakes have two important implications. First, these data serve as an important caution for using the composition of the bulk DOM pool to make inferences about the effects of DOM on within-lake processes. While macrophytic C is nearly undetectable in the DOM pools of our study lakes, it appears to be an important component of C cycling and energy flow in these systems. Second, our results indicate that these distinct DOM sources have very different effects on within-lake biological, chemical, and physical processes. For example, preferential uptake of macrophytic DOM has clear implications for microbial food web structure, particularly given the high growth efficiency of bacteria on this substrate (Findlay et al. 1986; Mann and Wetzel 1996; Tank 2009): once it enters the DOM pool, macrophytic organic matter could provide an important subsidy to higher trophic levels via a bacterial shunt (Waichman 1996). In macrophyte-rich Delta lakes, this could be particularly important, because algal photosynthesis is low (Squires et al. 2009). At the same time, because it is consumed rapidly, macrophytic DOM should play a modest role in the many physico-chemical processes that DOM is known to influence, such as light penetration and water chemistry (reviewed in Prairie [2008]). In contrast to macrophytic DOM, thermokarst-derived DOM accumulates in Delta lakes, indicating that it is less likely to provide energy to higher trophic levels. This has

also been described for temperate, watershed-derived allochthonous DOM (Cole et al. 2006), and in general, terrestrially derived DOM is not expected to support the rapid cycling characteristic of autochthonous organic matter (Kritzberg et al. 2006). However, the longer residence time of thermokarst-derived DOM likely allows for a greater influence on the physico-chemistry of this system.

Future changes expected across the Mackenzie Delta landscape could have clear repercussions for the composition of DOM in these lakes. Although only a small proportion of Delta lakes currently experience strong thermokarst effects, permafrost thawing is increasing across the north (ACIA 2004). The high-elevation lakes surrounded by the ice-rich permafrost necessary for thermokarst (Kokelj and Burn 2005) account for approximately 15% of total Delta lake area (Lesack and Marsh 2007). Thus, future permafrost degradation could markedly alter the DOM composition of many high-elevation Delta lakes. At the same time, springtime peak flood heights and the connection time of higher elevation lakes to the river appear to be decreasing because of the declining effects of river-ice breakup (Lesack and Marsh 2007). The resulting increased water clarity—particularly in mid-elevation lakes—could act to increase macrophyte densities in these waterbodies, while decreased connection times should cause inputs of river-water DOM to decline. Increased autochthonous, macrophytic DOM in some lakes and allochthonous, thermokarst-derived DOM in others could accentuate the differentiation that we currently observe between Delta lake types, creating clear classes of lakes that function very differently from one another as a result of their DOM source and composition.

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